AUGUST 8, 1983

CHEMICAL & ENGINEERING

NEWS

CHEMRAWN recommendations focus on world food supply
Page 23

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Chemicals for electronics

One of the strongest growth markets
Page 7

Cover: Surface detail of one of the new 256K RAM superchips made by Western Electric at Allentown, Pa.

Volume 61, Number 32
CENEAR 61 (32) 1–40
ISSN 0009-2347

CHEMICAL & ENGINEERING
NEWS
AUGUST 8, 1983

News of the Week

■ **U.S. and China sign bilateral trade agreement on import of Chinese textiles and apparel.** **Page 4**

■ **Monoclonal antibody kit allows physician to identify quickly bacteria causing meningitis.** **Page 4**

■ **Chemical industry productivity is gaining sharply in second-half 1983, reversing trend.** **Page 5**

■ **House/Senate conferees decide to end U.S. moratorium on new chemical weapons.** **Page 5**

Business

Outlook for titanium dioxide is good; a strong market is ahead, and possibly even a tightening of supply in a year. **Page 12**

International

Japanese petrochemical companies see improvement in second-half 1983, with help from the U.S.'s economic recovery. **Page 14**

Relative decline in U.S. pharmaceutical firms' R&D is endangering the drug industry's competitive position worldwide. **Page 15**

Government

National Science Foundation's chemistry division gets a pat on the back from outside advisory committee reviewers. **Page 20**

Science

Research leading to new technologies for pest control, crop yield, and soil improvement to feed the world's growing population recommended by CHEMRAWN II and NAS groups. **Page 23**

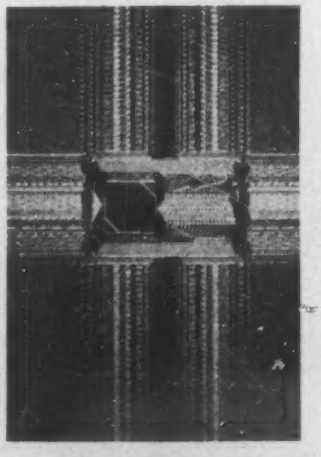
Technology

Process to grow high-strength carbon fibers found serendipitously during experiments at General Motors research lab. **Page 27**

Letters 2

Concentrates
Business 6
Government 18
Science/Technology 22

The Departments
ACS Comments 28
People 39
Newscripts 40



Cover Story

Chemicals for the high-flying electronics industry are enticing market, especially in resists for making new circuits. **Page 7**

Chemicals for Electronics: New Growth in Competitive Field

After low growth for three years, electronics chemicals are off and running again in high-technology race; biggest challenge is in photoresists

Stephen C. Stinson, C&EN New York

One of the premier targets for chemical companies in their drive for high-growth specialty markets in the 1980s is electronics. Activity is intense in both technology and marketing, with U.S. electronic chemical sales already totaling $2.4 billion. That figure could grow to $4.3 billion (deflated) in just five years.

The list of names in this field is notably diverse. The giants are there, including Airco, Air Products, Allied, Ashland Oil, Ciba-Geigy, Du Pont, Eastman Kodak, General Electric, W. R. Grace, Hercules, Monsanto, Union Carbide, and Westinghouse. But medium- and small-sized companies also are in abundance, such as J. T. Baker Chemical (part of Richardson-Vicks), Colonial Printing Ink (part of Millmaster Onyx), Dynachem (part of Morton Thiokol), Engelhard, Philip A. Hunt Chemical (majority owned by Olin), Shipley (minority owned by Rohm & Haas), UOP (part of Signal Cos.), and Wacker Siltronic.

Entry can be in many ways, since there are six major and seven minor product groups in electronic chemicals going to two major kinds of electronic applications (printed circuit boards and integrated circuits). But entry and survival aren't that easy; both take a heavy technical commitment, exemplified in such areas as the fast-changing photoresist market.

Now that the U.S. economic recovery apparently is fully under way, the electronics industry is rebounding from a three-year period of low growth, and with it, sales of chemicals and substrates needed to produce electronic components. This economic recovery comes at a time when suppliers and captive users of semiconductor integrated circuits must advance fabrication technology to make the next generation of higher-density chips for faster computers and other microprocessor-driven devices. Though development of the new fabrication technology will demand improvements in chemicals across the board, perhaps the greatest challenge for chemists will be to discover new polymers for use as resists (screening layers over substrates) to attain the higher resolution of features needed on semiconductor surfaces.

For the electronics industry, the recession began in 1980. The growth rate in sales and captive use of printed circuit boards in the U.S. fell to 4% from $2.7 billion in 1980 to $2.8 billion in 1981 after a 9% annual clip in the late 1970s. The rate slipped further in 1982, with printed circuit

Worldwide use of resists will forge ahead . . .

$ Millions (1980)	Sales and captive use 1980	1986	Average annual growth, %
UV screen inks	$ 17	$ 31	10%
Dry films	130	236	10
Liquids	79	210	18
TOTAL	$226	$477	13%

. . . with U.S. consuming the largest share . . .

Area			
U.S.	$125	$276	14%
Europe	59	106	10
Japan	42	95	15
TOTAL	$226	$477	13%

. . . and with microelectronics the fastest growing outlet

Use			
Printed circuit boards	$ 75	$144	12%
Microelectronics	41	121	20
Photochemical machining	9	11	4
TOTAL	$125	$276	14%

Source: R. M. Kossoff & Associates

Recovery will enlarge U.S. markets for electronic chemicals

$ Millions (1983)	Sales and captive use 1980	1983	1988	Average annual growth 1980–83	1983–88
APPLICATION					
Semiconductors	$1200	$1500	$2900	7.8%	14.0%
Printed circuit boards	800	900	1400	4.0	9.0
TOTAL	$2000	$2400	$4300	6.3%	12.4%
PRODUCT CLASS					
Substrates	$900	$1100		7.1	
Plating chemicals	200	200	2400	a	11.4
Photoresists	100	100		a	
Packaging materials	300	400		10.0	
Acids & etchants	100	100	1100	a	12.9
Atmospheric gases	100	100		a	
Other[b]	300	400	800	10.0	15.0
TOTAL	$2000	$2400	$4300	6.3%	12.4%

a Rate of growth relatively small. b Includes specialty gases, cleaners, dopants, auxiliary materials, photoresist adjuncts, solvents, and solder masks. Source: C. H. Kline & Co.

Glossary of electronic chemical and processing terms

Chemical vapor deposition. Deposition of silicon, silicon nitride, or doped silicon dioxide glass layers onto silicon wafers by high-temperature decomposition of appropriate gaseous compounds in a chamber.

Dry film resist. Photoresist for printed circuit boards containing a photoactive resin system between a polyethylene lower layer film and a polyethylene terephthalate upper layer, useful for defining lines and spaces less than 15 mils wide.

Integrated circuit. System of thousands of interconnected microscopic transistorlike regions formed in upper layers of wafers of such semiconductors as silicon.

Metal-oxide semiconductor (MOS). Substance whose functioning depends on the greater electrical conductivity of a metal-like silicon compared with its relatively insulating oxide; fabrication is aided by greater mobility of dopant atoms in the metal than in the oxide.

Negative resist. Resist whose solubility in the developer is greater for light-unexposed than exposed areas, leading to formation of patterns by removal of unexposed zones.

Phototool. Glass or photographic film master of resist resin pattern to be produced on a silicon wafer or printed circuit board substrate; used by exposing the resist through the phototool in contact with the resist, separated from it by a minute distance, or by projection from a greater distance.

Positive resist. Resist whose solubility in the developer is greater in light-exposed than in unexposed areas, leading to formation of patterns by removal of exposed areas.

Printed circuit board. Reinforced plastic laminate board bearing linear patterns of electrically conducting metal whose features may range from 2 to 100 mils in width; such boards serve as mounting and interconnection for integrated circuits, transistors, diodes, capacitors, and coils that complete an electronic device.

Resist. Resin applied by screening or photochemical imaging and development, whose function is to provide a patterned protecting layer over areas of a substrate that are not to be affected by a subsequent etching or plating step.

Screen inks. Resists screened in a pattern on the surface of a printed circuit board, which then are cured in place by heat or ultraviolet light; patterns are formed on screens from photomasks using photoresists; useful for defining lines and spaces from about 15 to 100 mils wide.

Solder mask. Photoactive resin applied by liquid coating or dry film techniques, followed by photochemical imaging and development to leave small holes in the resin coat over the surface of a printed circuit board, to protect circuit elements from solder flow; not removed from board after use, solder mask resins are formulated for hydrolysis and fire resistance to protect the board during its life.

VLSI (very-large-scale integration). Current density level of functional features called gates incorporated onto the same size chip, amounting to more than 1000 gates per chip; contrasted with medium-scale integration (MSI) of 10 to 100 gates per chip or large-scale integration (LSI) of 100 to 1000 gates that were thought satisfactory a few years ago.

boards amounting to only $2.9 billion. At the outset of renewed health, values of printed circuit boards may grow from 15 to 20% in 1983 to $3.3 billion to $3.4 billion, and settle down to a steady 9% per year average increase over the next five years.

This faltering and resumption of high growth rates in electronics has been mirrored by sales of substrate materials and processing chemicals to the industry. Analyst Chem J. Listner of C. H. Kline & Co., Fairfield, N.J., estimates sales for printed circuit boards were $800 million in 1980, increasing only 4% annually to $900 million in 1983. But he predicts a 9% yearly increase thereafter to $1.4 billion in 1988 in constant dollars. Similarly in semiconductors, Listner says substrate and chemical sales for this use grew at 8% per year from $1.2 billion in 1980 to $1.5 billion in 1983. But this advance will accelerate to an average 14% per year to $2.9 billion in 1988, also in constant dollars.

Listner adds that technology as well as economic growth will be important for the electronic chemicals industry in coming years. Kline has introduced a new service to clients to track worldwide strategic developments in electronic chemicals on a continuing basis. Topics will include patterns of geographic shift in electronic component production and packaging, with emphasis on the importance of Southeast Asia; photolithographic trends in the U.S., Europe, and Japan; strategies of successful chemical suppliers; trends in processing components; and market surveys of selected, high-growth, specialty chemicals.

To chemists, new technology will bring challenges in terms of new high-density semiconductor integrated circuit chips. The new chips are exemplified by so-called 256K random-access memory (RAM) chips, which actually contain 262,144 bits of memory on the same size chip used to make 64K, 16K, and earlier RAM devices. IBM already makes such chips for captive use. Western Electric Co. expects to begin marketing these memories on the merchant market in the fall of this year.

Because speed of signal transmission dictates overall computer speed, electronics firms push to crowd more functions onto chips of the same size. RAM chips are important, because these are high-volume items on which chip makers will cut their new technological teeth. Later, success in 256K RAM chips would allow semiconductor fabricators to use the same very-large-scale integration (VLSI) technology for microprocessors and other integrated circuit devices.

But successful VLSI fabrication means creating features on silicon wafer surfaces to resolutions of 1 μm (1 millionth of a meter). In a chip-making context, resolution means ±10% with uniformity over the area of work. These fine resolutions begin to approach the 320 to 430 nm (1 billionth of a meter) wavelengths of ultraviolet light used in photolitho-

graphic processes today. Intense effort is under way to develop methods that use shorter wavelengths. These methods include deep UV (less than 300 nm), electron beam, and x-ray. Use of such methods will need not only automated machines and optics but also new photosensitive polymers as resists.

Indeed, the whole field of resists for all electronic devices is the subject of vigorous research and competition. Richard M. Kossoff, president of the consulting firm of R. M. Kossoff & Associates, New York, N.Y., estimates that the U.S. market alone in resists will grow from $125 million in 1980 to $276 million in 1986 at 14% average annual increases.

Kossoff says that resists have been highly profitable products in the past, though competitive price cuts on similar types from the growing number of producers have led to erosion of margins. He expects high profitability to continue for resist producers who develop resin systems for the new, high-resolution technologies. Apparent high profits, plus increased demand in the current electronic revolution, will lead to an increase in the number of firms serving the worldwide market from 46 in 1980 to 65 in the late 1980s. Some of the new corporate entrants in the U.S. resist market will be Japanese firms, Kossoff says, which will form partnerships with U.S. companies, license U.S. producers, or sell in this country on their own.

Types of resists differ according to the type of electronic devices to be made. Resists come in three main types. Photolithography of long-established printed circuit boards in consumer goods such as radios at resolution of lines and spaces 10 to 40 mils wide (1 mil = 1 thousandth of an inch or about 25 μm) uses one type, called screen inks. Resolutions from 15 down to 4 mils or less for computers and telecommunications devices often require a second type of resist called dry films, though two companies are trying to displace dry films with their photoimaged liquid coatings. Semiconductor integrated circuit chips demanding ultrafine resolution use the third type of resist, called photoimaged liquids.

Chip makers who are trying to make 256 RAM chips with their superfine 1-μm resolutions now depend on existing liquid resists that were satisfactory for the 2- to 2.5-μm resolutions of earlier, less dense chips. But these fabricators realize the need for new resists for the new, short-wavelength techniques, and some chip makers are taking the lead in developing these polymers.

In the first type of resist, screen inks, three companies dominate the U.S. market. Colonial Printing Ink Co., East Rutherford, N.J., subsidiary of Millmaster Onyx Corp.; Dynachem Corp., Tustin, Calif., subsidiary of Morton Thiokol; and W. R. Grace's Polyfibron division, Lexington, Mass., sell almost 90% of the total. Printed circuit board producers form the image of the resist ink pattern to be laid down by photoimaging on a stainless steel mesh or synthetic fabric screen. Ink flows through unblocked spaces in the screen onto the board, where it is cured. In the late 1960s Dynachem developed a UV-curable screen ink. Dynachem president Vern Ownbey estimates that 60% of screen inks today are UV-cured, though the rest are still heat-cured. UV curing is valued for greater speed and less space taken up by curing equipment.

In the second type of resist, films for fine-line circuitry resolution on printed circuit boards have a photoresist resin system sandwiched between a polyethylene and polyethylene terephthalate film. The U.S. market is divided about equally by Dynachem and Du Pont's Riston Products division, Wilmington, Del., though Hercules' graphics systems division, Wilmington, has about 2%. Du Pont and Dynachem developed the product about the same time in the late 1960s, and Du Pont has licensed Dynachem on its patent for the idea of using the sandwich between films. Hercules has not taken a license and is the defendant in a suit by Du Pont.

Electronic chemicals comprise world of specialty products

The electronics industry consumes a rich variety of solid, liquid, and gaseous chemicals, all of which are much more costly than grades used in other industries because of elaborate purification to remove chemical impurities and filtration to exclude particulates. Processes begin with such substrates as single-crystal silicon wafers for integrated circuits and copper-clad reinforced plastic laminates for printed circuit boards. These need cleaners to prepare them for making devices.

Screening or photolithography of resist resins into patterns on substrates exposes some areas and protects others from chemical processes that follow. Photoresists need developers to form protective patterns; some resists require adhesion promoters in advance; and all resists must be removed with strippers after one fabricating step to open the way for the next.

Such atmospheric gases as oxygen form insulating silicon dioxide layers on silicon wafers. Nitrogen provides inert atmospheres or produces passivating silicon nitride layers on wafers close to the end of processing. Compounds of antimony, arsenic, boron, and phosphorus dope entire wafers or patterned regions into electron-rich or -deficient areas, creating microscopic transistors. Acids and etchants like ammonium bifluoride and hydrofluoric acid eat patterns into silicon dioxide layers; sulfuric acid and hydrogen peroxide strip off some resists. Vapors of silane derivatives react to form conducting polycrystalline silicon interconnections. Radio frequency generates plasmas from specialty gases like carbon tetrafluoride, sometimes with added oxygen, for dry etching of features on wafers or stripping of resists.

Electronics firms draw on all types of plating technology to connect devices to the outside world. Anodes and salts of aluminum, copper, gold, nickel, platinum, titanium, and tin-lead find use here, as well as associated chelating agents, activators, catalysts, and brighteners. On printed circuit boards, resistlike resins called solder masks limit flow of solder to desired areas, then remain laminated to the board as protective coating during its lifetime.

On completion of the printed circuit board or integrated circuit, ceramics, epoxies, silicones, and polyurethanes form protective coatings for finished devices.

Thirty U.S. firms are major chemical suppliers to electronics industry

	Substrates	Packaging	Photoresists and adjuncts	Plating chemicals	Gases	Process chemicals	Cleaners and other specialties	Dopants	Other[a]
Airco					X			X	
Air Products					X				
Alco Standard, Synthane Taylor division	X								
Allied	X		X	X		X		X	
Ashland Oil			X			X			
J. T. Baker Chemical[b]			X			X		X	
BBF, Polyclad Laminates division	X								
Adolph Coors		X							X
Du Pont	X		X			X	X		X
Engelhard				X					X
Fortin Laminating	X								
General Electric	X	X							
Philip A. Hunt[c]			X	X		X	X		
Kyocera[d]		X							X
MacDermid			X	X		X	X		X
Mica	X								
Monsanto	X								
Morton Thiokol		X	X	X			X	X	X
NGK Spark Plug		X							X
NVF	X								
Oak Industries	X								
Occidental Petroleum, Sel-Rex and Udylite divisions				X			X		X
Shin-Etsu Chemical	X								
Shipley			X	X		X	X		
Siltec	X	X							
Technic				X					
UOP, Norplex division[e]	X								
Union Carbide	X		X		X	X	X	X	X
Wacker Siltronic	X								
Westinghouse	X								

a Includes auxiliary chemicals and solder masks. b Subsidiary of Richardson-Vicks. c Owned 63.4% by Olin. d U.S. subsidiary of Kyoto Ceramic. e Part of Signal Cos. **Source:** C. H. Kline & Co.

Dry film users peel off the polyethylene film and laminate the bare resin surface to the board substrate. The resist resin is exposed by UV light with a photographic film master through the polyester film layer. On peeling off the polyester film, the resist pattern is developed, using organic solvent or alkaline aqueous-based developer. After the plating or etching operation with parts of the substrate protected by the resist, the resist is stripped off with organic or alkaline aqueous stripper.

Companies are reluctant to discuss dry film resist chemistry. The base resin could be methyl methacrylate copolymerized with methacrylic or itaconic acid to render it alkali-soluble. The base resin could be mixed with a monomer such as pentaerythritol triacrylate, and the whole system rendered photosensitive with an anthraquinone derivative. Exposure to UV light would cause polymerization of the monomer, enmeshing the base resin in a three-dimensional polymer network to resist dissolving by alkali. Thus the resist would be dissolved away only from unexposed areas.

Du Pont and Dynachem also have solder masks based on dry film technology. Solder masks are resists designed to produce a patterned protective cover with open areas at board holes and surrounding metal pad areas, to guide the flow of solder only to those areas. Solder masks are not stripped from boards after application of solder, but are formulated with resins and additives to give flame retardance and resistance to hydrolytic, mechanical, and heat damage to protect the board during its lifetime.

Carl S. Gates, director of Du Pont's Riston Products division, notes that exposure of dry film resists through polyester films sometimes causes image distortion. He says the company plans a new formulation that will eliminate the need for such films. Both Du Pont and Dynachem have introduced aqueous developers and strippers to eliminate needs for organic solvent recovery systems.

Gates says the company has been test marketing an integrated system that automatically cleans boards, peels film from resist, laminates resist to boards, and exposes circuit images onto resists, all without operator intervention. Du Pont will expand marketing of the system this year. Dynachem's Ownbey says that his firm will introduce an automated system that will take boards from cleaning through development of resist images early in 1984.

In the past two years, however, two companies have brought liquid resists and solder masks to market to compete with dry films for fine-line circuitry. Materials costs for the liquids are alleged to be one third of those for dry films, but suppliers will have to show that liquids are at least as easy to handle as dry films to compete successfully. Ownbey is skeptical about the future of liquids against dry films, but remarks that his company also has developed a liquid to enter the market, depending on how successful Ciba-Geigy and W. R. Grace are with theirs.

W. R. Grace's Polyfibron division is silent on the chemistry of its ma-

Twenty-two firms are major suppliers of photoresists for electronics production

Company	UV screen inks	Liquids		Dry films		
		Positive	Negative	Positive	Negative	Solder masks
Allied		X				
AZ Photoresist Products[a]		X				
J. T. Baker Chemical[b]		X	X			
Ciba-Geigy			X			
Colonial Printing Ink[c]	X					
Dynachem[d]	X	X	X		X	X
Du Pont					X	X
Eastman Kodak		X	X			
EM Chemicals			X			
Ethone[e]	X					
W. R. Grace	X		X			
Hercules						X
Philip A. Hunt[f]		X	X			
KTI[g]		X	X			
London Chemical[g]	X					
MacDermid	X	X				
Mead		X	X			
M&T Chemicals	X					
3M	X			X		
Norland Products			X			
Shipley[h]	X	X				
Wornow	X					

a Division of American Hoechst. b Subsidiary of Richardson-Vicks. c Subsidiary of Millmaster Onyx. d Subsidiary of Morton Thiokol. e Subsidiary of Asarco. f Owned 63.4% by Olin. g Subsidiary of Union Carbide. h Owned 30% by Rohm & Haas. **Source:** R. M. Kossoff & Associates

terials, but those of Ciba-Geigy's plastics and additives division, Hawthorne, N.Y., are based on photosensitive, heat-cured epoxies.

Gordon Buchi, who manages Ciba-Geigy's liquid resist business, says that base resin is made by condensation of epichlorohydrin, bisphenol A, and *p,p'*-bis(hydroxystyryl) ketone. The company's solder mask resin also contains copolymerized tetrabromobisphenol A as fire retardant. A cascading sheet of liquid coats cleaned, preheated boards passing under it. After drying of the resist film, it is exposed through a photomask. UV light causes cross-linking by [2+2] photocycloaddition reactions among unsaturated ketone units. Cyclohexanone dissolves away unexposed areas to develop the image. At this point, faulty boards can be stripped for reuse with 2-methoxy- or 2-ethoxyethanol or *N*-methylpyrrolidone. Otherwise, the board is heated to 275 °F for a final cure with a latent amidine hardener in the formulation. Thus, in contrast with most resists, the Ciba-Geigy material stays with the board.

Buchi explains that such a resist has the advantage of providing an epoxy coat that is compatible with epoxy laminations to follow in making boards. It also avoids stripping as an extra step, as well as treatment of

High thermal stability, sensitivity will be keys to success for electron beam resist candidates

	Sensitivity[a]	Glass transition temp., °C
POSITIVE RESISTS		
Methacrylates		
Polymethyl methacrylate	100	104
Polybutyl methacrylate	0.4	19
Polyphenyl methacrylate	150	110
Halogenated methacrylates		
Polytetrafluoropropyl dimethylmethacrylate	5	93
Polyhexafluorobutyl methacrylate	0.4	50
Polytetrafluoropropyl methacrylate-co-glycidyl methacrylate	0.4	65
Polytrifluoroethyl α-chloroacrylate	2.5	133
Polytrichloromethyl methacrylate	3.0	138
Cross-linked methacrylates		
Polymethyl methacrylate-co-methacrylic acid	20	150
Polymethyl methacrylate-co-methacrylic acid-co-methacryloyl chloride	20	140
Polymethyl methacrylate-co-*tert*-butyl methacrylate	1.6	131
Polyphenyl methacrylate-co-methacrylic acid	10	142
Polyolefin sulfones		
Poly(1-butene sulfone)	1.0	—
Poly(2-methyl-1-pentene sulfone)	4.0	—

	Reactivity[b]	Glass transition temp., °C
NEGATIVE RESISTS		
Epoxy and vinyl polymers		
Polyglycidyl methacrylate	0.028	78
Polyglycidyl methacrylate-co-ethyl acrylate	0.023	10
Polychlorohydroxypropyl methacrylate-co-dimethyl maleate	0.026	—
Diallyl phthalate	0.036	160
Vinyl-containing polydimethylsiloxane	0.2[a]	—
Halogenated aromatics		
Polystyrene	5.5	85
Poly(*p*-chlorostyrene)	0.28	122
Chloromethylated polystyrene	0.12	110
Iodinated polystyrene	0.42	156
Chloromethylated poly(α-methylstyrene)	0.23	170
Chloromethylated polynaphthyl methacrylate	0.28	113
Polyvinylnaphthalene-co-vinylbenzyl chloride	0.41	—
Polyvinylbenzyl chloride-co-glycidyl methacrylate	0.67	77
Polystyrene-containing tetrathiofulvalene units	6[a]	—

a Microcuries per sq cm. b Product of weight-average molecular weight and gel point radiation dose; sensitivities of negative electron beam resists are proportional to weight-average molecular weights. **Source:** Nippon Telegraph & Telephone Public Corp.

boards with possibly harsh organic solvent strippers.

Gerald Teplitzky, who is vice president for Grace's Letterflex business, says that the company sells automated machinery for cleaning, coating, exposing, and developing of boards. Ciba-Geigy has such a system for its liquid solder mask, with a manual step for exposure in the middle. The company sells only coating and developing units for its liquid resist.

Whereas photoimaged liquid, dry film, and screen ink resists for printed circuit boards are all of the negative type, both positive and negative liquid resists, the third overall type, find use in making semiconductor integrated circuits, with increasing emphasis on positive types. Developing negative resists dissolves away unexposed areas; exposed areas are dissolved away in positive ones. Philip M. Papoojian, marketing manager for electronic chemicals at J. T. Baker Chemical Co., Phillipsburg, N.J., estimates that positive resists for integrated circuits have 40 to 45% of that market now growing at 25 to 30% per year. Negative resists still have 55 to 60% of the market, Papoojian says, but annual growth will only pace the electronics industry itself at 10 to 15%.

Among the many firms who sell liquid resists for integrated circuits, three primary producers (one selling to formulators) have almost 90% of the U.S. market: Eastman Kodak's graphic arts division, Rochester, N.Y., Philip A. Hunt Chemical, Palisades Park, N.J., and Shipley Co., Newton, Mass. Eastman sells resist materials to other suppliers, such as J. T. Baker, which formulate them for sale to integrated circuit producers. In efforts to get into the integrated circuit resist market, Rohm & Haas bought a 30% interest in Shipley for $38 million in February 1982, and Olin Corp. paid $90 million the following December to acquire Turner & Newall Industries' 63% interest in Philip A. Hunt.

Although specific integrated circuit resist compositions are secret, many negative types are based on polyisoprene or polybutadiene, and some positive ones contain phenolic resins. Photosensitive additives in negative resists initiate cross-linking of double bonds in the base resin, making these exposed areas insoluble in developers. Derivatives of 2-diazo-1,2-naphthoquinone, mixed in relatively large amounts into phenolic novolacs, serve as dissolution inhibitors in these positive resists. Photolysis causes rearrangement of diazo compounds to 1-indenecarboxylic acid derivatives. Developing in aqueous alkali leaches phenolic resin and indenecarboxylate from exposed areas, while relatively nonpolar, unphotolyzed diazo compounds retard dissolving from unexposed zones.

One advantage of negative resists for integrated circuit production is good resistance to etching. Their greatest weakness, which is causing many electronics firms to switch over to positive resists, is poor resolution. Unlike dissolving of sugar in water, in which the solvent plucks molecules from a crystal surface, organic solvent developers for resinous resists must swell the polymer to leach uncross-linked chains out of the mass. Swelling is four to five times the 1-μm thickness of resist films. Negative resists also are sensitive to oxygen and must be used under nitrogen or vacuum.

In addition to better resolution, positive resists have the advantage of being imaged by projection rather than contact with the phototool (resist pattern). But positive resists have their faults. They are more expensive, less sensitive, poorer in adherence to substrate, and less forgiving during development. Solubility differences between exposed and unexposed regions are less for positive resists, requiring more attention to development conditions. □

Titanium dioxide heads for prosperity in 1984

Much of the pure white color in the world comes from the chemical titanium dioxide. Few substances dominate their use as does this durable inorganic pigment. It has competitors, but none are very big.

Unfortunately, as a business titanium dioxide has not had nearly the distinction as its application. Like synthetic fibers, titanium dioxide has wandered through most of the past decade trying to regain heights of the early 1970s. But also like synthetic fibers, the pigment finally may have a shot at good times.

Key Chemicals

Titanium dioxide may be close to the end of a long transition period extending from poor market years in the mid- and late 1970s through a plant shakeout in the next few years to a new series of strong market years. Remaining capacity is much higher quality now, with most old pollution problems under control. Markets are rebounding, especially in housing, and could see basic long-term growth in plastics.

In fact, industry analysts are beginning to wonder if supply of the product could become tight. Consider: If a few more very old sulfate-process plants close, the U.S. might need even greater net imports of titanium dioxide than it has now to meet demand. So far, that's no problem. European producers are eager to send over material while their economies are still weak. But in a few more years, there might not be enough surplus product in Europe to export. Adding to the squeeze in the U.S. could be rising U.S. titanium dioxide exports. They're going up strongly this year, and marketing people think they'll continue to rise after 1983.

The leading U.S. use of titanium dioxide, hard-surface coatings such as house paint, might have only minimal long-term growth, say industry analysts. But the pigment's use is rising an estimated 7% a year in pigmentation of fabricated plastics such as building siding.

As yet, U.S. producers haven't reacted to such forecasts with plant expansion beyond small debottlenecking programs. A major new plant is very expensive because of complex processing and doesn't yet seem justified.

For the immediate market outlook, see the following page.

Bruce Greek, Houston

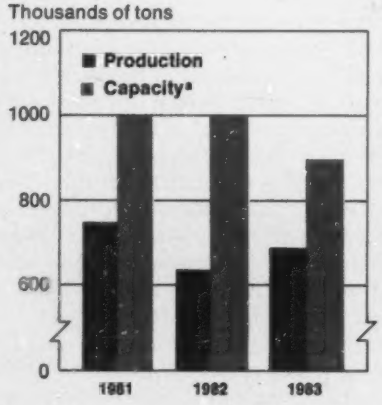
Key Chemicals

Titanium Dioxide

TiO_2

- ***Production recovering***
- ***Capacity down***
- ***Prices holding***

PRODUCTION/CAPACITY



[a] First quarter.

HOW MADE

Recovery from natural or synthetic ores using chlorine or sulfuric acid

MAJOR END USES (U.S.)

Hard-surface coatings 50%, paper coatings and fillers 25%, plastics and rubber fillers 15%, ceramics 5%

FOREIGN TRADE

Exports—rising to 80,000 tons in 1983, imports—rising to 175,000 tons in 1983

PRICES

Anatase form 69 to 70 cents per lb; rutile form 75 cents; discounting modest

COMMERCIAL VALUE

$950 million for production, 1983

The dominant white pigment, titanium dioxide, may have bright prospects ahead, but producers are having to take about one patient year to get there. For 1983, the product has to pick itself up from a worse than expected recession and move toward tighter capacity use. To date, the year has been just about what producers need to get on their new profits springboard.

Like most big-volume inorganics produced in the U.S., titanium dioxide usually doesn't move very fast. But production first nosedived 17% in 1982 and then about-faced for an expected 8% rebound in 1983. Meanwhile, one old plant was closed (NL Industries' at Sayreville, N.J.) and another was sold (Gulf + Western's at Ashtabula, Ohio, to SCM). Both imports and exports increased significantly. About the only thing that didn't change was the list price.

For the rest of 1983 and early 1984, the outlook for titanium dioxide continues upward as the economy improves. Most titanium dioxide used in the U.S. goes eventually into housing, automobiles, and paper—all consumer products now showing strong increases in demand. For 1983, titanium dioxide production probably will come close to 700,000 tons, well above 640,000 tons in 1982. However, 1983 production still will be below the recent high of 750,000 tons in 1981.

Plant capacity for titanium dioxide has dropped, levering up operating rates. With the closing of NL Industries' plant in late 1982, U.S. nameplate capacity declined to a bit more than 900,000 tons per year from the former 1 million tons. Even with some production lines not operating, a conservative estimate on 1983 production of 690,000 tons gives an operating rate of more than 75% of nameplate capacity. Effective capacity to make titanium dioxide reaches no more than 90% of nameplate, perhaps less, because of the complexity of the processing steps. So the effective operating rate is heading over 85%.

NL Industries' exit as a U.S. producer doesn't mean that its former production will all go to other U.S. producers. Imports have risen this year about 25% and might reach 175,000 tons, with an important part from NL's European operations.

Imports are somewhat offset by exports of titanium dioxide. In 1983, exports seem sure to reach 80,000 tons (up 14%) and possibly 90,000 tons (up 29%) if developing countries' economies recover and crude oil prices remain a reduced burden on these economies.

The surplus of imports over exports in 1983 could be as low as 65,000 tons if imports falter and exports boom, possibly pushing U.S. production higher than anticipated. If demand continues up as the recovery rolls along, supply of titanium dioxide might even start to tighten. Paint-maker SCM (Glidden) may have had this in mind with its plant purchase. Although the seasonal peak in paint demand usually would be over now for ordinary house painting, demand still is surprisingly strong for titanium dioxide. A wet spring seems to have pushed timing back, keeping up demand for trade (retail paint) sales deeper into summer than usual. Demand for paint in the fall also may be stronger than normal.

Housing and other "hard surface" coatings demand makes up about half the total market for titanium dioxide. The other half is dominated by paper coatings and fillers and by plastics and rubber colorants and fillers. The economic recovery boosts demand for higher-quality coated papers in many ways, for example in advertising pages and increased subscriptions in publications.

In another sphere, plastics are perhaps the best growth area for titanium dioxide demand even though they account for just 15% of the total. New developments such as plastic-film grocery bags to replace paper bags will help titanium dioxide, used in printing on the sacks.

Given another year for such new growth in plastics, coupled with recovery demand in paper and surface coatings, titanium dioxide could climb to well over 80% of nameplate capacity use, approaching the maximum U.S. plants can turn out. Since little new capacity is due, 1984 could move producers into the healthy profits stance they have waited so long to achieve. And companies might finally have to face a positive sort of challenge they haven't had in a long time—the need to consider an expensive major addition to capacity.

Drop in U.S. share of drug R&D endangers world position

Richard J. Seltzer, C&EN Washington

For decades, the U.S. pharmaceutical industry has been one of the most profitable and rapidly growing sectors of the U.S. economy. Together with other high-technology industries, it has played an important role in generating exports and trade surpluses. It continually has expanded its output, productivity, and employment, while holding price increases below the rate of inflation.

The pharmaceutical industry thus has maintained an image of immunity from the deteriorating international competitive position besetting other once robust U.S. industries such as autos, steel, textiles, machine tools, and consumer electronics.

However, warns a report just released by a National Academy of Engineering panel, "This image is apparently exaggerated, and probably false." The U.S. share of the world pharmaceutical market (measured in terms of sales and of introduction of new drugs) is still relatively stable—after a decline in the 1960s—despite growing competition from foreign producers; but the U.S. share of world pharmaceutical production and exports is only half what it was in the early 1960s. And most important, data compiled by the panel show the U.S. pharmaceutical industry suffering "a clear relative deterioration in the foundation of pharmaceutical competitive position—the research efforts necessary for discovery and introduction of new patented drugs."

The situation is thus one of relatively good health now, but there is a poor prognosis for the future. The panel, therefore, seeks in its report to answer taree questions:

- What changes have occurred in the U.S.'s competitive position in the multinational pharmaceutical industry?
- Why have these changes occurred?
- What government policy steps can counteract the relative decline?

The study is entitled "The Competitive Status of the U.S. Pharmaceutical Industry: The Influences of Technology in Determining International Industrial Competitive Advantage." It is one in a series of seven reports on the international competitive status of specific U.S. industries prepared for NAE's Committee on Technology & International Economic & Trade Issues.

Chairman of the high-powered, 13-member pharmaceutical panel is Charles C. Edwards, president of Scripps Clinic and Research Foundation, and the rapporteur is Lacy G. Thomas, a professor at Columbia University's Graduate School of Business. Panel members include William N. Hubbard Jr., president of Upjohn; Lewis H. Sarett, a retired senior vice president of Merck; William M. Wardell, professor of pharmacology at University of Rochester Medical Center; Richard D. Wood, chairman and chief executive officer at Eli Lilly; and Alejandro Zaffaroni, chairman and chief executive officer of Alza Corp.

The study focuses on patented drugs and does not cover over-the-counter medicines or generic products. About 150 firms conduct research for and produce patented drugs in the U.S. Only 20 of them have significant U.S.-based multinational operations; about 20 more are U.S.-located operations of foreign-owned multinationals. The remaining firms have largely domestic sales, and some have only small research labs.

The panel points out that the importance of research and innovation for competition among major world pharmaceutical firms puts the industry in a select grouping of high-technology industries. Drug companies invest high proportions of sales and profits in R&D (more than 50% of profits, for example), and spend relatively high amounts on basic research (about 12% of U.S. pharmaceutical research is basic). There is also relatively little government financing of industrial R&D. These three trends rarely are present simultaneously in other industries.

To recoup their fast-rising expenditures for developing new drugs, major pharmaceutical firms have increasingly needed to sell their new products on a worldwide scale. Since most pharmaceutical innovations are not successful commercially, the firms depend on a handful of successful innovations. For example, in 1979, their three best-selling products provided two thirds or more of total U.S. pharmaceutical sales for each of four major drug firms. Thus, failure to produce a steady stream of new products—to replace those that lose market share to imitators or on which the 17-year-long patents expire—ultimately would be devastating to a pharmaceutical firm. Turnover is rapid. For instance, only four of the 30 top selling products in 1965 remained in the top 30 by 1980.

On the basis of their innovation, U.S. firms were predominant in world markets from 1950 to 1960, accounting for a large majority of research spending and new products,

U.S. share of world drug R&D down more than half

	1964		1973		1978	
	R&D spending ($ millions)	World share, %	R&D spending ($ millions)	World share, %	R&D spending ($ millions)	World share, %
U.S.	$282	60%	$640	34%	$1159	28%
West Germany	40	8	310	16	750	18
Switzerland	38	8	244	13	700[a]	17
Japan	27	6	236	13	641	15
France	28	6	166	9	328	8
U.K.	29	6	105	6	332	8
Italy	15	3	82	4	147	4
Sweden	9	2	33	2	72	1
Netherlands	9	2	26	1	72[a]	1

a Estimated. **Note:** Data are in current dollars and represent spending for both human and veterinary research. **Source:** Organization for Economic Cooperation & Development

more than half world pharmaceutical production, and a third of international trade in medicinals. U.S. pre-eminence continued, although to a lesser degree, through the 1960s. However, since then the competitive advantage of U.S. firms "has been not only reduced, but apparently eliminated"—especially in the earliest phases of the discovery and development process. And this despite U.S. pre-eminence in basic biomedical research, and enormous U.S. government expenditures for biomedical research and health care.

Thus, the U.S. share in the world has been constant or declining since 1960 for each of six aspects of competitive industrial performance the panel considered: research effort, innovation, production, sales, market structure, and exports. The U.S. decline is not one in absolute terms, the panel emphasizes, but rather a result of slower growth rates than foreign competitors.

For instance, the U.S. share of world pharmaceutical R&D spending has fallen from 60% in 1964 to less than half this in 1982. Moreover, drug R&D spending (in constant value local currency) rose only 1.1% a year in the U.S. in the 1970s, while it was growing 13.1% in the U.K., 8.1% in Japan, and 7.9% in West Germany.

Meanwhile, the products of innovation—U.S.-owned new drugs entering clinical trials in the U.S.—have dropped steadily in number from a yearly average of 60 in the mid-1960s to about 25 a year in 1982. By contrast, foreign-owned drugs undergoing similar trials have remained almost constant at about 20 per year.

This decline in U.S. new-drug introduction does not reflect merely a decline in basic pharmaceutical innovation, the panel points out. The soaring expenses of premarket testing have forced firms to be much more selective of compounds to be tested clinically, and to be brought to market. These testing costs have risen faster in the U.S. than elsewhere.

Thus, in the U.S. the average cost per new drug (in constant 1980 dollars) has risen from about $6.5 million before 1962 to about $44.7 million in 1980 (excluding the cost of capital), primarily because of greater requirements for clinical and toxicology testing. The average R&D expenditure per drug, including capital cost, is estimated at $70 million. The average total time for clinical testing and drug marketing approval in the U.S. is in excess of eight years. Indeed, the panel notes, it now may take more than 15 years from initiation of basic research on a pharmacological problem to marketing of a new product.

Turning to another criterion for international competitiveness, the panel points out that the U.S. share of world pharmaceutical production has plummeted from 50% in 1962 to 38% in 1968 and 27% in 1978. U.S.-based production has been relatively stable, rising 5% a year in 1965–75. But West European and Japanese competitors raised production 15% a year. Meanwhile, U.S.-owned firms increased their production overseas much more rapidly than their domestic production, growing from $700 million overseas in 1963 to more than $6 billion in 1978. By 1978, overseas production accounted for 40% of the U.S. multinational total.

Two basic changes have occurred in the world pharmaceutical market structure during the past two decades—greater concentration of innovation among larger firms, and increasing internationalization of the industry. Both trends have important implications for U.S. competitiveness. First of all, not surprisingly, sharply rising costs of innovation are forcing smaller U.S. firms out of the game. This makes them increasingly

NAE probes relation of innovation to U.S. competitiveness

How can U.S. industry be made more competitive in world markets? A key factor is its ability to innovate new technology, notes chemist N. Bruce Hannay, foreign secretary of the National Academy of Engineering, who retired last year as vice president for research and patents at Bell Laboratories.

Hannay has set this issue as a major focus of his service since 1976 as NAE foreign secretary. He chairs a Committee on Technology & International Economic & Trade Issues, sponsored by NAE and by the National Research Council's Commission on Engineering & Technical Systems. The just-released report on the international competitive status of the U.S. pharmaceutical industry is but one link in the committee's ongoing study of relationships between technological innovation and productivity and the ability of U.S. industry to compete in international trade.

In the first phase of its work, the committee produced a report and four monographs. Published in 1978, the report, "Technology, Trade, and the U.S. Economy," indicates that the innovation process in the U.S. is not so vigorous as it used to be. The four monographs provide a more detailed examination of U.S. government policies and practices affecting technological innovation. They include: "The International Technology Transfer Process," "The Impact of Regulation on Industrial Innovation," "The Impact of Tax and Financial Regulatory Policies on Industrial Innovation," and "Antitrust, Uncertainty, and Technological Innovation." (All are available from the NAE foreign secretary's office.)

The second phase of the committee's work is a set of seven studies, each prepared by a panel with expertise on a specific industry. Published last year and earlier this year have been reports on the international competitive status of the auto industry, machine tools industry, and the fibers, textiles, and apparel industry (C&EN, May 9, page 5). Still to come after the pharmaceutical report are studies covering the electronics industry (slated for September), ferrous metals (November), and civilian aviation (January).

The objective of the seven studies is to identify global shifts in industrial technological capacity on a sector-by-sector basis; relate these shifts in international competitive advantage to technological and other factors; and assess prospects for further technological change and industrial development. The panel preparing each study also suggests a series of policy options for consideration by public and private policy makers. Besides experts serving on the panels, outside specialists, government officials, and Congressional staff members also are consulted.

dependent on licensing new products from foreign firms instead of developing new drugs themselves. It also makes them prime targets for takeover by foreign firms seeking entry to the U.S. market.

During the 1970s, European pharmaceutical firms established a broad multinational base in the U.S. market that in the near future will be used for direct marketing in the U.S. of European pharmaceutical innovations. Should Japanese firms attempt to make a similar entry to the U.S. market, the panel points out, fewer appropriate small firms will now be available.

Why have these changes occurred in the U.S.'s competitive position? The panel identifies two sources: factors general to the U.S. economy, and causes specific to the pharmaceutical industry. The report notes that there are numerous similarities between the drop in pharmaceutical industry competitiveness and the relative decline of the U.S. economy and of other U.S. industries, including other high-technology industries, compared to Japan and Western Europe.

However, the panel emphasizes, in two respects the pharmaceutical industry's competitive position has declined more severely than other U.S. industries, because of factors unique to the industry. First, there has been a "precipitous drop" in the proportion of world drug production located in the U.S., "a decline wholly unmatched in other segments of the chemical industry."

The explanation is more rapid growth of demand for pharmaceuticals abroad than in the U.S., coupled with widespread foreign nontariff barriers (such as discriminatory safety and pricing policies) that effectively require domestic production. Major U.S. firms have adapted by building production facilities abroad. Thus, the decline in worldwide sales is much less severe than the drop in U.S.-located production. But it means loss of jobs and income in the U.S.

A second and even more important trend unique to the industry is the drop in the U.S. share of world pharmaceutical R&D spending by half, "markedly more severe" than for any other U.S. industry. By contrast, the U.S. share of world chemical R&D spending has fallen only a few per cent. The panel concludes government policies are the most likely cause—"both U.S. government policies that relatively discourage pharmaceutical innovation and foreign policies that relatively encourage innovation abroad."

The panel therefore suggests several policy steps to counteract the decline in U.S. competitiveness. In the trade area, it suggests development of "an appropriate U.S. response" to foreign trade (nontariff) barriers favoring their domestic products. It also suggests changing Food & Drug Administration policy prohibiting the export of new drugs not yet approved for sale in the U.S.—even if already approved abroad—thus giving U.S. firms an incentive to transfer pharmaceutical technology abroad and produce the new drugs there. Such new drugs could be exported as finished chemicals not specifically labeled for new drug use, it notes.

In the patent area, the panel suggests legislation to restore the time lost from the 17-year life of a patent as a result of FDA regulatory requirements. The report suggests reconsidering antitrust policy to determine if it discourages mergers of small and midsize firms that would make U.S. pharmaceutical firms more competitive globally. The panel also proposes expansion of research tax credits to include research-related expenditures not now covered.

The panel says that the impact of product liability rules on the industry and its innovation should be studied to try to reduce "this disincentive to research." And in the regulatory area, the panel supports implementation by FDA by administrative action, as rapidly as possible, of recent recommendations by the Commission on the Federal Drug Approval Process to speed up the drug testing and approval process.

Copies of the 106-page report can be obtained for $8.95 prepaid from the National Academy Press, 2101 Constitution Ave., N.W., Washington, D.C. 20418. The project was supported by a grant from the National Science Foundation. □

Japanese a growing force in world drug industry

In its study of the U.S. pharmaceutical industry's international competitiveness, the National Academy of Engineering panel tried to assess prospects for technological change and future industrial development. One major trend it points to is the growing innovational significance of Japanese pharmaceutical firms.

Traditionally, Japan has not been a significant presence in world pharmaceutical markets, the report notes, because Japanese firms were not successful at innovation. In its development stage, the country's pharmaceutical industry focused on building domestic generic-type production, behind effective protective barriers against foreign imports, and was imitative rather than innovative.

However, since the mid-1970s, the approach has changed. R&D spending is increasing greatly (up from 6% of world pharmaceutical R&D spending in 1964 to 15% in 1978, for example). Moreover, the Japanese government has adopted policies providing incentives for research and innovation, and for international expansion.

The outcome of Japanese corporate and government policies is only now becoming visible in the world market, the panel notes—but the changes are "quite dramatic." For example, in 1981, Japanese firms ranked first in major new drugs introduced to world markets, with 17 out of 65 products. U.S. firms were second, with 13.

Furthermore, in 1982, Japanese firms obtained more than 16% of U.S. patents for pharmaceuticals and medicinal products, up from previous levels (2% in 1963, 6% in 1973, 9% in 1979). Japan received 38% of U.S. medicinal patents to foreign firms in 1982.

In addition, Japanese pharmaceutical firms are forming joint ventures with U.S. firms to market Japanese discoveries. Prominent are links between Abbott and Takeda, and Fujisama and SmithKline. "These linkages are clearly first steps toward direct marketing of Japanese products overseas," the panel notes.